

REINVESTIGATION OF THE NI AND CO METAL-SILICATE PARTITIONING. Ph. Kegler¹, A. Holzheid², D.C. Rubie³, D. Frost³ and H. Palme¹, ¹Universität Köln, Institut für Mineralogie und Geochemie, 50674 Köln, Germany, philip.kegler@uni-koeln.de, ²Universität Münster, Institut für Mineralogie, 48149 Münster, Germany. ³Universität Bayreuth, Bayrisches Geoinstitut, 95440 Bayreuth, Germany

Introduction: The earth and the other terrestrial planets as well as differentiated asteroids contain an Fe-rich metallic core that segregated from mantle silicate shortly after or during accretion [1, 2]. One consequence of the formation of a metal core is that siderophile elements (e.g. Fe, Ni, Co, Ge, PGEs) are strongly partitioned into the core and are therefore depleted in the mantle. The extent of depletion contains information on details of the core forming process [3]. The partitioning of an element (el) between metal and silicate can be described by exchange metal-silicate partition coefficients, K_D^{el-Fe} , defined as

$$K_D^{el-Fe} = D_{met/sil}^{el} / D_{met/sil}^{Fe}$$

with $D_{met/sil}^{el} = C_{met}^{el} / C_{sil}^{el}$ (C=concentration by weight). The K_D^{Ni-Fe} at one atmosphere and 1400°C is around 400 [4], reflecting the strong siderophile character of Ni at these conditions. At 5 to 10 GPa and 2000°C the K_D^{Ni-Fe} has decreased to around 20 [5]. Extrapolation of the high pressure data of [5] to 1 atm would produce a K_D^{Ni-Fe} of, at maximum, 50. Temperature is in part responsible for this difference. Recalculation of the K_D^{Ni-Fe} of 1 atm and 1400°C to 2000°C yields a value of 90, based on data by [4]. This is still about a factor of two higher than highest possible high pressure extrapolation (Fig.1). To clarify this discrepancy, additional Ni and Co partitioning experiments at low pressures and high temperatures were performed. A more accurate set of data on the temperature and pressure dependence of K_D^{Ni-Fe} and K_D^{Co-Fe} will allow to disentangle the effects of temperature and pressure.

Experiments: Experiments were done within the range of 1 atm to 10 GPa at temperatures between 1300 and 1900°C. The experiments were performed with vertical gas mixing furnaces at the Universität Köln (1 atm), by using a piston cylinder apparatus at the Universität Münster and Bayrisches Geoinstitut (0.3-3.5 GPa) and by using multi anvil presses at Bayrisches Geoinstitut (3.5-10 GPa).

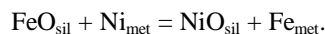
An Fe₅₄Ni₂₉Co₁₇ alloy was equilibrated with a silicate melt of basaltic composition. At lower pressures and temperatures (1 atm - 2.5 GPa, T= 1400-1440°C) the silicate melt was inserted into a crucible made of the investigated alloy. Because the increase of the melting point of silicates is twice that of the increase of the melting point of the alloy used, single crystal MgO crucibles were used as containers for the silicate and

metal phases at pressures above 2.5 GPa (T= 1460-1900°C) to enable liquid silicate - liquid metal equilibration. Post-run microprobe analyses of the silicate showed that the MgO of the crucible has only a very small effect on the silicate melt composition. In addition, the activities of NiO and CoO in silicate melts do not depend on the MgO content of the silicate within a fairly large range [5]. The experimental charges were analyzed using a Jeol 8900RL electron microprobe (Universität Köln). Operating conditions for silicate glasses were 20 kV, 600 nA and a defocused beam (raster size 20 µm). Counting times were up to 600 sec (Ni, Co), giving detection limits of 50 ppm for NiO and CoO. Metal phases were analyzed with 20 kV and 25 nA and a focused beam. Counting times were 60 sec. We were able to reduce the analytical uncertainties of calculated K_D^{Ni-Fe} and K_D^{Co-Fe} to 5%.

Results: Results are presented in Table 1 and shown in Figure 1. All data plotted in Fig. 1 are recalculated to 2000°C by using the 1 atm temperature dependence of K_D^{Ni-Fe} and K_D^{Co-Fe} [4]. The residual pattern plotted in Fig. 1 shows a much stronger pressure dependence of K_D^{Ni-Fe} and K_D^{Co-Fe} at pressures below 3 GPa, than at pressures above 3 GPa. At the higher pressures results agree within error with [5] and [6], although linear fits to log K_D vs P are less steep than those reported by [5] (see Fig. 1). The steep decrease of the Ni and Co K_D s with increasing pressure is not an artifact of improper temperature extrapolation. The K_D^{Ni} at 1400°C decreases with increasing pressure from 346 at 0.3 GPa to 91.4 at 2.5 GPa (Table 1, data for 1400°C)) clearly demonstrating that there is a very strong pressure effect at low absolute pressures.

Discussion: Two fits were made to the data in Fig. 1, one for all data below 3 GPa and one for data above 3 GPa. The slope of the fit for the high pressure data where the Li and Agee [5] and the Ito et al. [6] data are included is much less steep than that originally proposed by [5]. Using these new data and the corresponding correlations a crossover of K_D^{Ni-Fe} and K_D^{Co-Fe} vs pressure as suggested by [5] would not occur within the pressure regime of the Earth's mantle. This would have important consequences for models of core-mantle equilibrium.

The two pressure regimes for the exchange partition coefficients of Ni and Co require a change with pressure of the molar volume of the exchange reaction



and the same reaction for Co. A change in the coordination number of Co^{2+} and Ni^{2+} in silicate melts with increasing pressure has been suggested by [7-9]. This could produce the required change in molar volumes at about 3 GPa.

More experiments at pressures above 5 GPa will be performed to better define the slope of the decreasing K_D with increasing pressure. Attempts will also be

made to define the temperature dependence of the two K_D s at higher pressures.

References: [1] Lee, D.C. & Halliday, A.N. (1997) *Nature*, 388, 854-857. [2] Kleine, T. et al. (2002) *Nature*, 418, 952-955. [3] Walter M.J. et al. (2000) *In: Origin of the Earth and Moon* (eds. R. Canup and K. Righter), pp. 235-289. [4] Holzheid A. & Palme H. (1996) *GCA*, 60, 1181-1193. [5] Li J. & Agee C.B. (1996) *Nature*, 381, 686-689. [6] Ito et al. (1998) *AGU Monograph*, 101, 215-225. [7] Kepler, H. (1992) *Am. Miner.*, 77, 62-75. [8] Nelson, C. & White, W.B. (1986) *J. Mat. Res.*, 1, 130-138. [9] Kepler, H. & Rubie, D.C. (1993) *Nature*, 364, 54-55.

Table 1:

Sample	P [GPa]	T [°C]	Ni [ppm]		Co [ppm]		Fe [ppm]		$K_D^{\text{Ni-Fe}}$ ⁽³⁾	$K_D^{\text{Co-Fe}}$ ⁽³⁾
			silicate ⁽¹⁾	metal ⁽²⁾	silicate ⁽¹⁾	metal ⁽²⁾	silicate ⁽¹⁾	metal ⁽²⁾		
BKPCM 6	0.3	1400	58	296600	538	173800	35680	526200	90.7	18.0
BKPCM 1	0.5	1400	79	299900	848	175300	49480	531000	93.3	15.9
BKPCM 4	1.0	1400	144	300900	858	175400	50520	531700	66.1	16.0
BKPCM 5	1.5	1420	75	296900	562	173300	28530	518800	60.5	14.1
BKPCM 8	2.5	1440	379	305500	1615	177700	51890	514700	24.0	9.3
BKPCB 3	2.5	1460	157	276800	596	169100	24440	531300	25.3	11.0
BKHP 1	5.0	1600	270	308000	730	176300	14700	514400	14.7	6.1
BKHP5	5.0	1700	312	296500	1000	177600	19250	524600	19.8	6.0
BKHP 2	7.0	1720	599	293600	1360	172200	22130	525800	12.2	4.9
BKHP 7	7.0	1720	352	298400	1158	175000	21910	519300	21.1	5.9

(1) standard deviation at values < 100 ppm max. 15%, at values > 100 ppm max. 10%; (2) standard deviation max. 1%; (3) recalculated to 2000°C using experimental determined temperature dependences of $K_D^{\text{Ni-Fe}}$ and $K_D^{\text{Co-Fe}}$ at 1 atm. [4].

Fig. 1: Exchange coefficients $K_D^{\text{Ni-Fe}}$ and $K_D^{\text{Co-Fe}}$ as function of pressure

